

[54] **AROMATIC BIS
SULFONAMIDE-CONTAINING NYLON OR
POLYESTER**

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[52] **U.S. Cl. 524/169**

[58] **Field of Search 524/169; 564/90**

[56] **References Cited**

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[57] **ABSTRACT**

Described are thermoplastic polymers (e.g., nylon) containing an aromatic bis-sulfonamide having at least two aromatic rings and from 14 to 30 carbon atoms in the molecule in quantity sufficient to improve the melt flow properties of the polymer. These sulfonamides are of advantage in that they have relatively low volatilities at polymer processing temperatures.

11 Claims, No Drawings

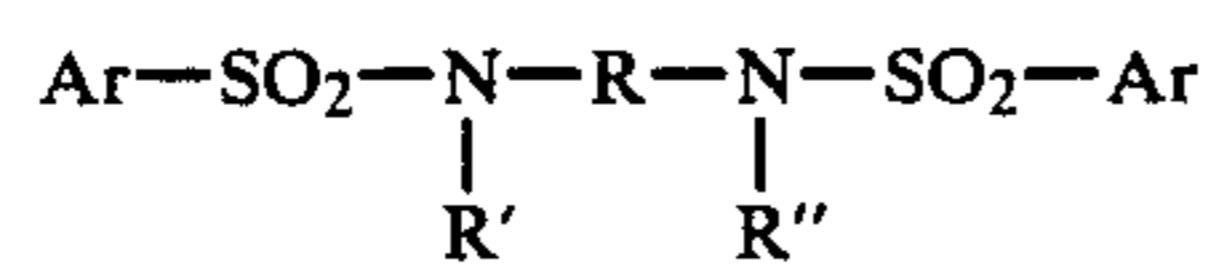
AROMATIC BIS SULFONAMIDE-CONTAINING NYLON OR POLYESTER

This invention provides thermoplastic polymer compositions having improved melt flow characteristics by virtue of the incorporation therein of certain sulfonamide plasticizers. Preferred additives also contribute flame retardancy to the polymers in which they are blended. The sulfonamides used pursuant to this invention have relatively low volatilities at polymer processing temperatures and thus minimize the extent to which the additive is vaporized during polymer processing. This in turn reduces the extent to which ambient air quality is impaired during processing.

As is well known, good polymer melt flow is an important property, as polymer formulations having inadequate flow properties can give rise to burning and incomplete article formation during molding operations.

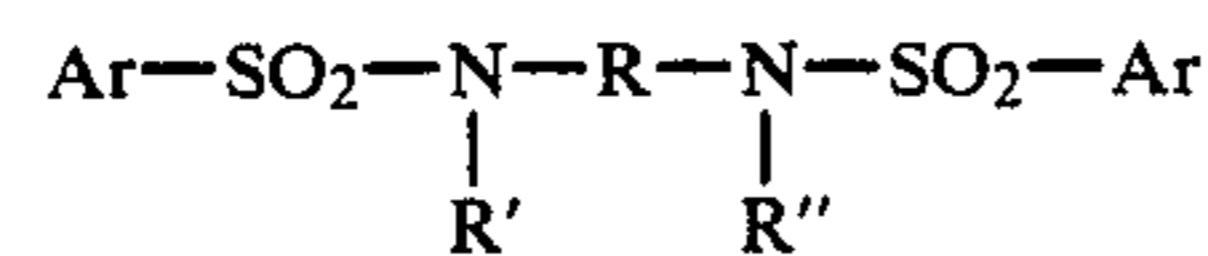
The sulfonamide used as additives pursuant to this invention are aromatic bis-sulfonamides containing at least two aromatic rings (preferably two or three) and from 14 to 30 carbon atoms (preferably 18 to 24) in the molecule. In a preferred embodiment these aromatic bis-sulfonamides contain from 1 to 14 and most preferably from 6 to 14 halogen atoms (preferably chlorine and most preferably bromine). The presence of such halogen atoms, especially when present as aromatic ring substituents, tends to enhance the thermal stability and flame retardant characteristics of the additive.

Among the aromatic bis-sulfonamides utilized pursuant to this invention are those represented by the general formula



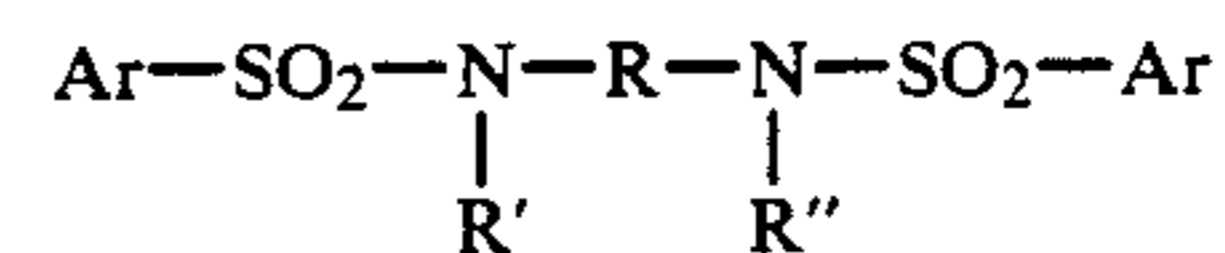
where Ar are the same or different aromatic or haloaromatic groups, R is a divalent hydrocarbon or halo-hydrocarbon group, and R' and R'' are independently hydrogen atoms or hydrocarbon groups. Most preferably the two Ar groups are both the same as each other, and R' and R'' are identical to each other.

One preferred type of aromatic bis-sulfonamides utilized pursuant to this invention are halogen-free compounds which may be represented by the general formula



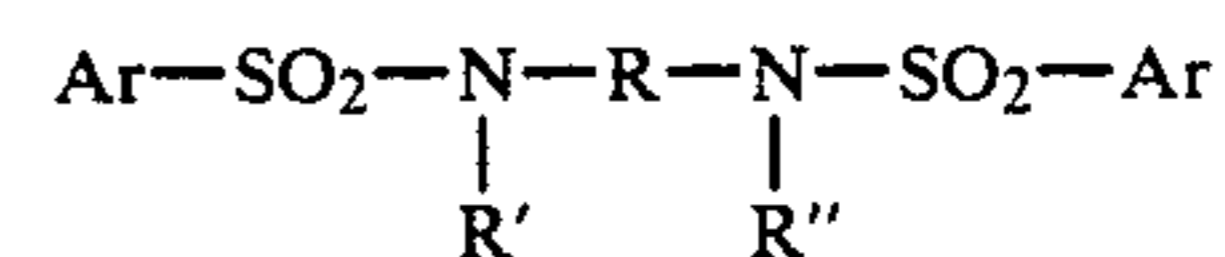
where each Ar group is a mononuclear aryl group having 6 to 10 carbon atoms, R is an alkylene group having from 1 to 8 carbon atoms, and R' and R'' are identical to each other and are hydrogen or alkyl groups each having up to 12 carbon atoms, and preferably up to about 8 carbon atoms.

Another preferred type of aromatic bis-sulfonamides utilized pursuant to this invention are halogen-free compounds which may be represented by the general formula



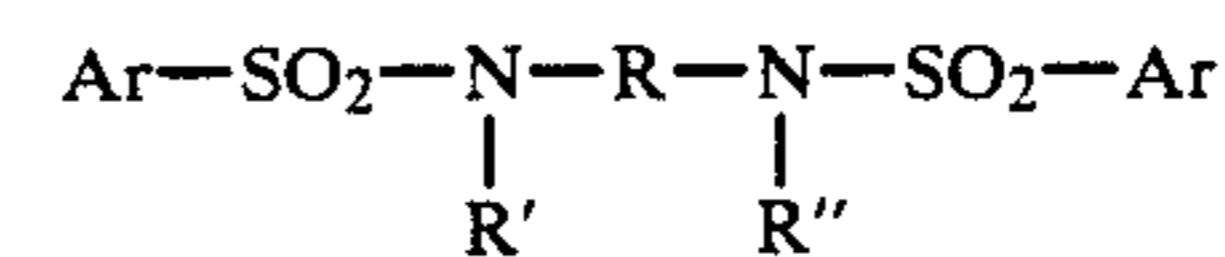
where each Ar group is a mononuclear aryl group having 6 to 10 carbon atoms, R is a cycloalkylene group having from 6 to 10 carbon atoms, and R' and R'' are identical to each other and are hydrogen or alkyl groups each having up to 12 carbon atoms, and preferably up to about 8 carbon atoms.

Still another preferred type of aromatic bis-sulfonamides utilized pursuant to this invention are halogen-free compounds which may be represented by the general formula



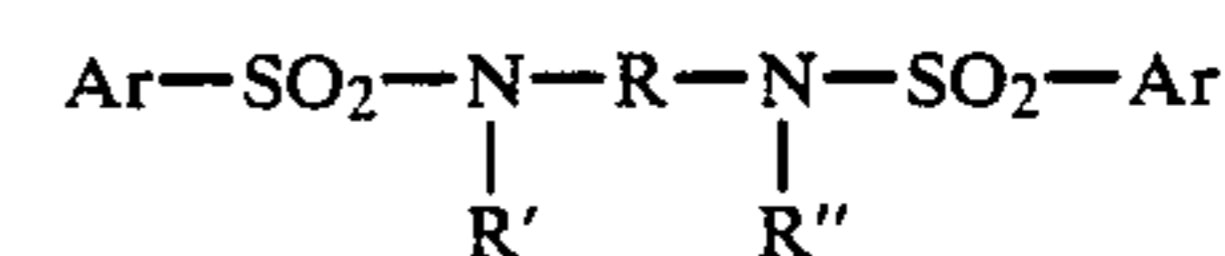
where each Ar group is a mononuclear aryl group having 6 to 10 carbon atoms, R is an arylene group having from 6 to 10 carbon atoms, and R' and R'' are identical to each other and are hydrogen or alkyl groups each having up to 12 carbon atoms, and preferably up to about 8 carbon atoms.

One preferred type of halogen-containing aromatic bis-sulfonamides utilized pursuant to this invention are compounds which may be represented by the general formula



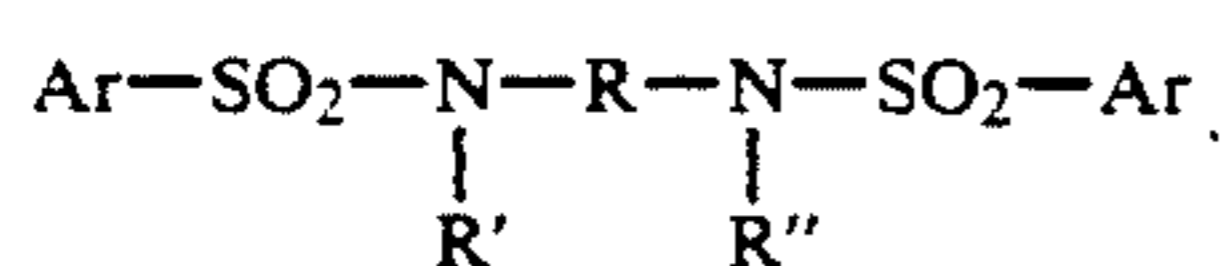
where each Ar group is a mononuclear aryl group having 6 to 10 carbon atoms and from 1 to 5 halogen atoms (preferably chlorine or bromine or both), and most preferably having 3 to 5 bromine atoms, R is an alkylene group having from 1 to 8 carbon atoms, and R' and R'' are identical to each other and are hydrogen or alkyl groups each having up to 12 carbon atoms, and preferably up to about 8 carbon atoms.

Another preferred type of halogen-containing aromatic bis-sulfonamides utilized pursuant to this invention are compounds represented by the general formula



where each Ar group is a mononuclear aryl group having 6 to 10 carbon atoms and from 1 to 5 halogen atoms (preferably chlorine or bromine or both), and most preferably having 3 to 5 bromine atoms, R is a cycloalkylene group having from 6 to 10 carbon atoms, and R' and R'' are identical to each other and are hydrogen or alkyl groups each having up to 12 carbon atoms, and preferably up to about 8 carbon atoms.

Still another preferred type of halogen-containing aromatic bis-sulfonamides utilized pursuant to this invention are compounds which may be represented by the general formula



where each Ar group is a mononuclear aryl group having 6 to 10 carbon atoms and from 1 to 5 halogen atoms (preferably chlorine or bromine or both), and most preferably having 3 to 5 bromine atoms, R is an arylene group having from 6 to 10 carbon atoms, and R' and R'' are identical to each other and are hydrogen or alkyl groups each having up to 12 carbon atoms, and preferably up to about 8 carbon atoms.

A few illustrative additives useful in the practice of this invention include

N,N'-p-cyclohexylenebis(benzenesulfonamide),
 N,N'-o-phenylenebis(benzenesulfonamide),
 N,N'-p-phenylenebis(benzenesulfonamide),
 N,N'-hexamethylenebis(4-chlorobenzenesulfonamide),
 N,N'-hexamethylenebis(4-bromobenzenesulfonamide),
 N,N'-hexamethylenebis(2,5-dichlorobenzenesulfonamide),
 N,N'-hexamethylenebis(2,4,5-trichlorobenzenesulfonamide),
 N,N'-hexamethylenebis(2,4,5-tribromobenzenesulfonamide),
 N,N'-ethylenebis(benzenesulfonamide),
 N,N'-ethylenebis(2,5-dichlorobenzenesulfonamide),
 N,N'-ethylenebis(4-bromobenzenesulfonamide),
 N,N'-ethylenebis(2,4,5-trichlorobenzenesulfonamide),
 N,N'-(1,2,3,4-tetrahydro-1,4-naphthalenediyl)bis(4-bromobenzenesulfonamide),
 N,N'-1,2-ethanediylbis[2,5-dibromo-N-ethylbenzenesulfonamide],
 N,N'-(9,10-dihydro-9,10-anthracenediyl)bis[N-methylbenzenesulfonamide],
 N,N'-(9,10-dihydro-9,10-anthracenediyl)bis[4-chloro-N-methylbenzenesulfonamide],
 N,N'-p-phenylenebis(2,4,5-tribromobenzenesulfonamide),
 N,N'-p-phenylenebis(2,3,4,5-tetrabromobenzenesulfonamide),
 N,N'-p-phenylenebis(pentabromobenzenesulfonamide),
 and
 N,N'-(dibromo-p-phenylene)bis(tribromobenzenesulfonamide).

General methods which can be utilized for the preparation of the additives used pursuant to this invention are known and reported in the literature. The most common procedure is to react an aromatic sulfonyl halide with an aliphatic, cycloaliphatic or aromatic diamine. The halogen-containing aromatic bis-sulfonamides may be formed either by utilizing an aromatic sulfonyl halide having one or more halogen atoms on the ring or by subjecting a halogen-free aromatic bis-sulfonamide to chlorination or bromination under usual conditions for effecting substitutive ring halogenation of aromatic hydrocarbons. For further details concerning applicable synthesis procedures, see for example Holmsen, U. S. Pat. No. 3,281,233; Kirsanov, et al., *Zh. Obshch. Khim.*, 1962, Vol. 32, 887-92; El-Hewehi, et al., *J. Prakt. Chem.*, 1962, Vol. 16 No. 5-6, 297-336; El-Hewehi, et al., *J. Prakt. Chem.*, 1966, Vol. 34 No. 5-6, 218-242, and Kuliev, *Dokl. Akad. Nauk Az. SSR*, 1976, Vol. 32(4), 25-29, all disclosures of which are incorporated herein by reference.

A wide variety of thermoplastic condensation polymers may be used in forming the compositions of this invention. Included are such thermoplastics as polyam-

ides (all types of nylons such as nylon 3, nylon 4, nylon 6, nylon 6,6, nylon 6,10, nylon 6,12, nylon 7, nylon 8, nylon 11, nylon 12, nylon 12,12 etc.), polyesters (e.g., polyethylene terephthalate, polybutylene terephthalate, etc.), polycarbonates, polyphenylene oxides either singly or in blends with polystyrenes (both rubber-free and rubber-modified), and the like. Preferred polymers are the nylons, particularly nylon 6 (polycaprolactam), nylon 6,6 (the polyamide of hexamethylene diamine and adipic acid), nylon 12 (polylauro lactam), and nylon 12,12 (the polyamide of lauro lactam and dodecandioic acid).

The concentration of the aromatic bis-sulfonamides used will of course dependent to some extent upon the identity and properties of the substrate thermoplastic polymer and of the particular additive system being employed therein, as well as the properties desired in the finished product. Generally speaking, however the polymer will normally contain an amount of aromatic bis-sulfonamide falling in the range of from about 2 to about 20, and preferably from about 2 to about 10, parts by weight per hundred parts by weight of the total thermoplastic composition. However departures from these ranges are entirely permissible and are within the ambit of this invention. Those skilled in the art can readily determine optimal proportions by the simple expedient of performing a few simple tests with the materials selected for use.

Methods for blending the additives into the substrate polymers are conventional and well known to those skilled in the art.

The advantages of employing aromatic bis-sulfonamides in the manner of this invention is illustrated by the enhanced thermal stabilities of typical aromatic bis-sulfonamides as compared to typical aromatic mono-sulfonamides of the type normally used as plasticizers in nylon. In a series of experiments, thermogravimetric thermal decomposition onset values of such materials were as follows:

N,N'-ethylenebis(benzenesulfonamide)	357.1° C.
N,N'-hexamethylenebis(benzenesulfonamide)	399.5° C.
N-ethylbenzenesulfonamide	217.7° C.
N-propylbenzenesulfonamide	224.1° C.
N-isopropylbenzenesulfonamide	220.1° C.
N-cyclohexylbenzenesulfonamide	220.9° C.

The improvements achievable in melt flow characteristics were illustrated in experiments employing a commercially available nylon-6,6 (ZYTEL resin), containing tetradecabromodiphenoxybenzene (SAYTEX 120 flame retardant) and antimony oxide, in the weight proportions of 81% nylon, 14% tetradecabromodiphenoxybenzene and 5% antimony oxide. Melt index and heat deflection temperature (HDT) determinations on this polymer with and without a sulfonamide of this invention are shown in the following table.

Sulfonamide	Amount	Melt Index, g per 10 min. 275° C./550 g ASTM D 1238	HDT, °C. at 264 psi ASTM D 648
None	None	7.1	249
N,N'-Ethylenebis-(benzenesulfonamide)	3%	8.5	247
N,N'-p-Phenylenebis-(benzenesulfonamide)	3%	58.9	238

-continued

Sulfonamide	Amount	Melt Index,	HDT, °C.
		g per 10 min. 275° C./550 g ASTM D 1238	at 264 psi ASTM D 648
N,N'-Hexamethylenebis- (benzenesulfonamide)	3%	22.1	240

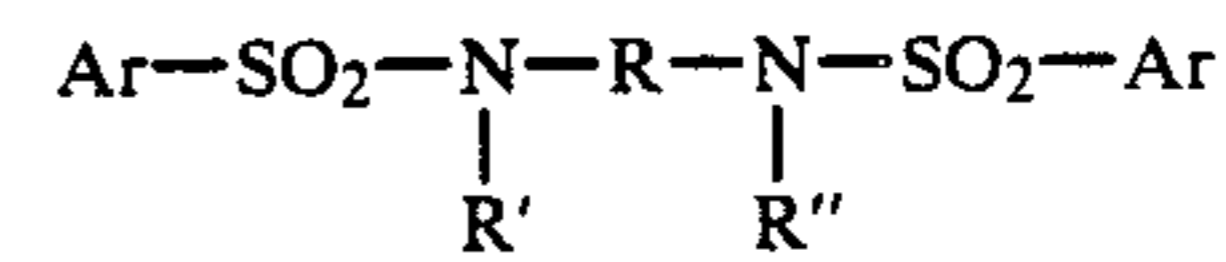
It will be noted that the N,N'-ethylenebis(benzenesulfonamide) increased the melt index only slightly whereas two of the preferred additives of this invention (i.e., those containing at least 18 carbon atoms in the molecule) gave substantial improvements in melt flow with essentially no sacrifice in heat deflection temperature.

Other conventionally used additives such as reinforcing fillers, fibers, pigments, mold release agents, nucleating agents, flame retardants, flame retardant synergists (antimony oxide, zinc borate, ferric oxide etc.), heat stabilizers, U.V. stabilizers, antioxidants and the like may be included in the compositions of this invention. Such additives may be employed in their customary concentrations. The use of conventional halogenated flame retardants may be reduced or eliminated when employing an aromatic bis-sulfonamide of this invention containing from 6 to 14 bromine and/or chlorine atoms per molecule. A particularly preferred additive complement, especially for use in nylon containing a halogen-free aromatic bis-sulfonamide of this invention, is the combination of tetradecabromodiphenoxybenzene and antimony oxide wherein the polymer contains from about 10 to about 15 weight percent of the tetradecabromodiphenoxybenzene and from about 3 to about 6 weight percent of the antimony oxide.

This invention is susceptible to considerable variation in its practice within the spirit and scope of the appended claims.

What is claimed is:

1. A polyamide or polyester polymer containing an aromatic bis-sulfonamide wherein the aromatic bis-sulfonamide is represented by the general formula



where each Ar group is a mononuclear aryl group having 6 to 10 carbon atoms and from 1 to 5 bromine atoms, R is an alkylene, a cycloalkylene, or an arylene group having from 6 to 10 carbon atoms, and R' and R'' are identical to each other and are hydrogen or alkyl groups each having up to 12 carbon atoms.

2. A composition of claim 1 wherein each Ar group contains 3 to 5 bromine atoms.

3. A composition of claim 1 contains 1 to 4 chlorine and/or bromine atoms.

4. A composition of claim 1 wherein each Ar group contains 3 to 5 bromine atoms and wherein R contains 1 to 4 chlorine and/or bromine atoms.

5. Nylon containing an aromatic bis-sulfonamide having at least two aromatic rings and from 14 to 30 carbon atoms in the molecule in quantity sufficient to improve, the melt flow properties of the polymer.

6. A composition of claim 5 wherein the aromatic bis-sulfonamide has two aromatic rings and from 18 to 24 carbon atoms in the molecule.

7. A composition of claim 6 wherein the sulfonamide is N,N'-p-phenylenebis(benzenesulfonamide).

8. A composition of claim 6 wherein the sulfonamide is N,N'-hexamethylenebis(benzenesulfonamide).

9. A composition of claim 6 wherein the nylon is nylon 6,6.

10. A composition of claim 6 wherein the nylon is nylon 6,6 and wherein the sulfonamide is N,N'-p-phenylenebis(benzenesulfonamide).

11. A composition of claim 6 wherein the nylon is nylon 6,6 and wherein the sulfonamide is N,N'-hexamethylenebis(benzenesulfonamide).

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